UDC 666.6.3:536.376

CREEP IN CERAMICS AND REFRACTORIES

V. S. Bakunov[1] and A. V. Belyakov[1]

Processes accompanying creep in ceramics and refractories are considered. Structural defects can be ranked according to their effect on creep (in descending order): macropores; low-melting phase inclusions, especially of vitreous phase; micropores; crystal boundaries, especially passing via micropores; block boundaries, dislocations; vacancies. The sequence is determined by intensity of diffusion mass transfer, i.e., the concentration of vacancies near the structural elements (defects) listed.

High-temperature creep in ceramics and refractories is caused by irreversible and nonequilibrium diffusion processes [1], which is related to a more complex composition and structure of oxide materials at the level of elementary cells and micro- and macrostructure compared with metals. Indeed, two or more types of ions, which differ in their radii and values and signs of their charges, create elementary cells of substantial volumes consisting of several sublattices. Due to such structure of the crystalline lattice and its defects responsible for plasticity (dislocations, boundaries, etc.), the geometry of defect sliding surfaces is very complicated, which virtually stops their migration. Furthermore, ceramics have a multi-level fractal type of structure [2], which also impedes processes of cooperative mass transfer: as a rule, ceramics are polycrystalline solids consisting of several phases, including a vitreous phase and pores.

It should be noted that systematic studies of creep in ceramics and refractories were first started at the D. I. Mendeleev Russian Chemical Engineering University under the guidance of D. N. Poluboyarinov, head of the Department of Chemical Engineering of Ceramics and Refractories [3] and for a long time the department has had a leading position in this field of research. The present study attempts to present broad outlines of deformation in such materials, staring with simple compositions, i.e. mono-oxide densely sintered ceramics and ending with the most complex materials: industrially produced refractories. This analysis is based on an extensive database of experimental data on the behavior of ceramics and refractories at high temperatures under mechanical loads registered with the same equipment [3 – 5]. This facilitates correlation of results. The study was performed based on special series of model samples prepared according to the same technology, moreover, in each series only one structure parameter varied. In testing densely sintered ceramics, the effect of additives, size of crystals (including sizes after thermal aging), quantity of the second high-melting phase and the vitreous phase was studied; in porous ceramics, the effect of the size or the shape of pores and the effect of porosity were separately investigated. In testing refractories, data on the effect of the phase composition, the role of the grog component and the binder, molding pressure, heat treatment temperature, molding method, etc. were obtained.

Interpretation of results was based on the concept of physical chemistry of crystals with defects and physics of open systems [6, 7]. The physicochemical approach makes it possible to specify elementary acts determining the deformation processes, depending on the composition and structure of materials. According to principles of physics of open systems, supply of mechanical energy to a material leads to its self-organization using existent structures or developing new structures for energy dissipation (dissipative structures [8]).

Experimental data obtained in [4] on creep in ceramics well agree with all process specifics ensuing from the diffusion model [9]: rectilinear kinetics of deformation, proportionality of the creep velocity to applied stress and the inverse proportion to the square or cube of the size of crystal, a correlation between creep activation energy and diffusion. Experiments carried out according to a specially developed method [10] enabling to determine a particular mechanism in a complex process and the range of its effect in a space of variables (temperature, load, crystal size) using mathematical statistic methods demonstrated the validity of such conclusions: the limiting role at high temperatures belongs to diffusion models [11].

Energy dissipation in diffusion creep takes place due to deformation by means of establishing local diffusion flows between single sites of the interface of heterogeneous materials [12]. In the case of vacancy diffusion, local oversatu-

---

[1] Institute of High Energy Density (IHED), Integrated Institute of High Temperatures, Russian Academy of Sciences, Moscow, Russia; D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

ration of vacancies $\Delta\xi_v$ related to heterogeneous distribution of normal stresses σ_n will be as follows:

$$\Delta\xi_v \approx \frac{\xi_0 \Delta\mu}{kT} = \frac{\xi_0 \Omega\sigma_n}{kT},$$

where ξ_0 is an equilibrium vacancy concentration at temperature T; $\Delta\mu = \Omega\sigma_n$ is the variation of chemical potential; Ω is the atomic volume; k is the Boltzmann constant.

In this case the diffusion coefficient D is determined by the vacancy diffusion coefficient D_v:

$$D = \Delta\xi_v D_v.$$

The sources and outlets for vacancies in the model considered are the body surfaces : outer and inner (pores), as well as crystal or block boundaries, dislocations, their effect sharply decreasing in the order listed. The most energy-consuming process is diffusion of vacancies over the volume of a crystal before reaching a boundary, whose permeability is significantly higher, i.e. $D_{boun} > D_{vol}$. The temperature dependence of the diffusion coefficient is set by the Arrhenius equation, where the value of activation energy is the sum of the energies of formation U and migration ω of vacancies [6]. Migration energy is differentiated as volume migration ω_{vol} and migration along crystal boundaries ω_{boun} ($\omega_{vol} > \omega_{boun}$), as well as along other interfaces and dislocations.

The following types of points defects are usually considered depending on their origin: intrinsic, thermally activated; impurity and nonstoichiometric defects. The processes of their formation are described by quasi-chemical disordering reactions in accordance with chemical thermodynamic and kinetic laws. Due to a low vacancy concentration, the model of approximation of diluted solutions is usually chosen. The reactions of formation of intrinsic defects are related to thermal fluctuation and require substantial energy consumption, accordingly, their concentration is usually very low. The formation of impurity and nonstoichiometric vacancies proceeds easily, and their quantity correlates with a content of heterovalent impurities or the degree of deviation from stoichiometry [6].

Available experimental data [4], taking into account general concepts described above, in this particular case suggest the following conclusions. The presence of a fixed substantial amount of impurities produces a constant concentration of vacancies within a rather wide temperature interval, which is not correlated with thermal fluctuations. The diffusion activation energy in this case contains just the mobility component and the process velocity grows in proportion to a quantity of impurity vacancies. Figure 1 shows (as a temperature dependence) the results of determining the velocity of deformation in especially pure corundum ceramics and, for reference purposes, in technical ceramics. It can be seen that a decrease in impurity concentration only decreases the process velocity, whereas its activation energy remains constant
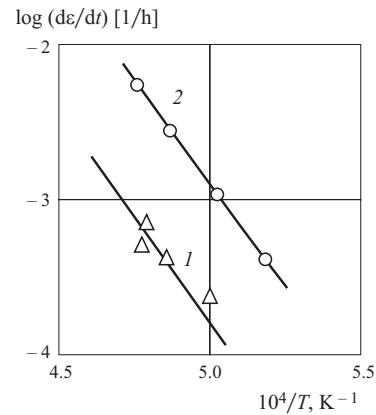

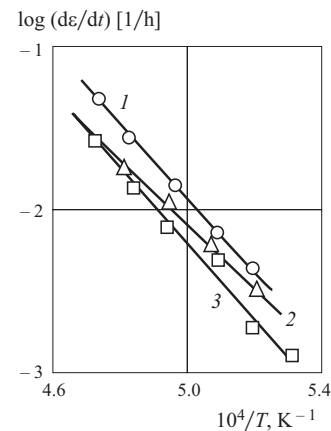**Fig. 1.** Creep velocity in corundum ceramics of extra (*1*) and technical (*2*) purity; load 2.5 MPa.

Fig. 2. Creep velocity in corundum ceramics (*1*) and ceramics with additives of 1 wt.% TiO_2 (*2*) and 0.3 wt.% MgO (*3*); load 1.3 MPa.

(the crystal sizes of ceramic samples are approximately equal).

An excess or deficit of oxygen with a deviation from stoichiometry acts similarly to impurities and forms respective vacancies. Thus, Fig. 2 shows the temperature dependence of creep velocity in pure corundum ceramics and ceramics with additives of magnesium and titanium oxides, i.e., metals with a higher and a lower degree of oxidation than aluminum. It can be seen that variations in the quantity of impurity vacancies in a narrow range in materials of the technical grade of purity has virtually no effect either on the process velocity, or on activation energy, i.e., introduction of additional impurities in small quantities does not influence the process. It can be assumed that in a relatively narrow temperature interval, in which creep in technical ceramics is usually measured, the same constant deformation mechanism will be registered for a particular material, which will be equal to the sum of defects present, which is corroborated experimentally. This established a certain value for the process activation energy.
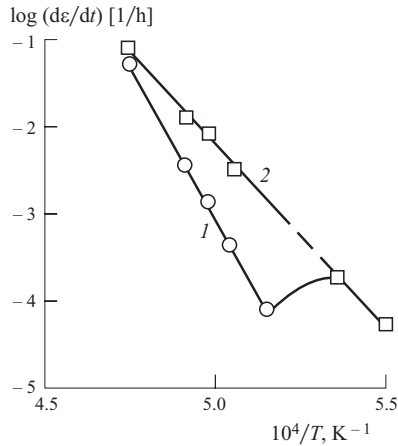
log (dε/d*t*) [1/h]

Fig. 3. Temperature dependence of deformation rate of densely sintered mullite ceramics in intervals of 1500 – 1800°C (*1*) and 1650 – 1800°C (*2*); load 2.5 MPa.

log (dε/d*t*) [1/h]

Fig. 4. Creep velocity in corundum ceramics with prevailing crystal size 10 (*1*), 30 (*2*), and 40 μm (*3*); load 1.3 MPa.

However, inflections in temperature dependence curves are possible due to modifications in material structure and related modifications in the creep mechanism. Thus, the temperature course of creep velocity for synthesized mullite ceramics in an interval of 1600 – 1650°C has an inflection: before and after this inflection the curve in coordinates $\log(d\varepsilon/d\tau) - 1/T$ is rectilinear (Fig. 3). When testing started above the abnormal behavior temperature, the dependence represented a continuation of the low-temperature segment. Such behavior was accounted for by a change in the composition of mullite during relatively long-term creep tests [4, 13].

It appears that the role of impurity and nonstoichiometric defects in creep of the types of ceramics used in practice that have a rather high impurity content (including metals with a variable degree of oxidation) is crucial, since the solution of thermally activated intrinsic vacancies has a very high degree of dilution even around the melting point. However, impurity and nonstoichiometric vacancies only contribute to self-diffusion of intrinsic ions, their contribution to mass transfer is insignificant due to their low quantity compared to the number of lattice points. They modify the process velocity, but activation energy depends on the mobility of intrinsic defects. This is corroborated by data obtained for various types of oxide ceramics [4].

The grid of crystal boundaries has a great effect on the creep process [12]. It is assumed that in densely sintered polycrystalline ceramics with the size of structural elements below $1 - 10$ μm, the number of lattice points in a purely volumetric state (on which the boundary has little effect) is insignificant, and diffusion is implemented along the boundaries or, more precisely, along boundary zones of width δ with the diffusion coefficient D_{boun}. Accordingly, expressions describing the creep velocity dε/dτ are, respectively:
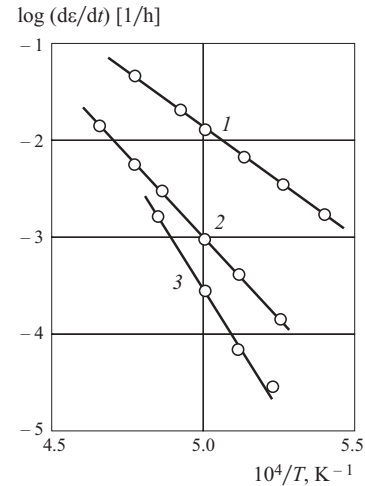
for volumetric diffusion mechanism:

$$\frac{d\varepsilon}{d\tau} = \frac{D_{vol}\,\Omega\sigma_n}{kTl^2};$$

for boundary diffusion mechanism:

$$\frac{d\varepsilon}{d\tau} = \frac{D_{boun}\,\Omega\sigma_n}{kTl^2},$$

where l is the characteristic distance between the sources and the outlets of vacancies (i.e., the size of crystals).

Assuming the volumetric and boundary mass flows to be additive, the effective diffusion coefficient is:

$$D_{ef} = D_{vol}\left(1 + \frac{D_{boun}\,\delta}{D_{vol}\,l}\right).$$

With $l < l_{cr} \approx D_{boun}\,\delta/D_{vol}\,l$, the mechanism of boundary diffusion will be crucial, with $l \gg l_{cr}$, volume diffusion will be decisive. Thus, a crystal is the element of a dissipative structure.

The state of the crystal boundary grid, the shape and size of crystals depend on the whole prehistory of ceramic manufacture, since it can be regarded as evolution of elements of a structure (from an atom to the whole product) [2]. Fixation of the final structure of a ceramic product takes place in firing as a result of diffusion processes. In firing pores are removed from the intermediate article, the in the final stage crystals grow and become cleared of impurities and micropores. The important factor is that in this process the concentration and mobility of vacancies change and the diffusion path from sources to outlets changes as well [15], whereas the part of the material through which the migrating boundary passes is perfected to a greater degree. Judging from experimental data (Fig. 4), the creep velocity decreases with growth of

crystals and the process activation energy grows, which is due to a decreasing role of impurity centers and a decreasing effect of boundary diffusion. Thus, the behavior of materials in relatively short-time creep tests is determined by their structure formed in firing. However, in passing to long-term tests, the situation changes.

Under high temperatures, two simultaneous processes take place in the field of external mechanical loads, which have different motive forces, but both produce a modification of the material structure. One is due to excessive free energy of the polycrystalline body related to the presence of various lattice defects (point, linear, surface, volumetric). The crystal tends to eliminate these defects, as a consequence, it grows, i.e., recrystallizes. Simultaneously with recrystallization, the crystal volume in the course of boundary migration is purified from impurities and micropores, and these defects become accumulated on inner interfaces and in cavities. On the whole the process is known as thermal aging, during which evolution typical of the final sintering stage take place. Another process is proper creep under the effect of external force as a consequence of vacancies flowing from sources to outlets. The first process under high-temperature treatment gradually modifies the structure of material, which affects the creep mechanism and the process velocity. Figure 5 shows the temperature dependence of the creep velocity in corundum ceramics before and after thermal aging. It can be seen that with increasing temperature and treatment duration (with growing crystal sizes etc.) the process velocity decreases and its activation energy grows. Similarly to samples not subjected to aging (Fig. 4), these results are due to a decreased content of impurity centers and a decreased effect of boundary diffusion.

Since the aging process kinetics is extended due to a small motive force, modifications of the structure are very slow. With short terms of creep tests, they are in fact imperceptible and only constant mechanism are registered, which correlates with the initial state of material. However, with long-term creep tests, these changes become perceptible, which is usually registered in service. An example in Fig. 6 schematically represents the structure of a sample of densely sintered corundum ceramics at far stages of creep preceding destruction [16]. In bending tests, cavities, cracks, and pores are observed in the stretched zone (a layer exists in the compressed zone, in which surface chips are sometimes observed). This is presumably related to coagulation of vacancies predominantly on micropores, microcracks, and dislocations existing before testing. All processes occur in the established creep stage, i.e., the deformation mechanism remains depending on diffusion; destruction occurs suddenly without acceleration of the deflection. It should be noted that these modifications of the structure are results of the summary effect under thermal activation of aging, i.e., surface tension forces and creep as external force. They are registered in experiments with simple objects, i.e., densely sintered oxide ceramics. In other cases the situation is complicated by the
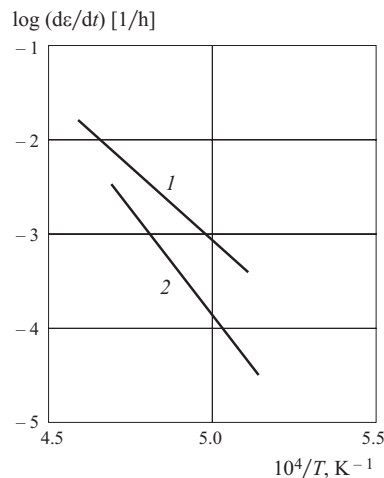

Fig. 5. Creep in initial corundum ceramic samples (*1*) and after thermal aging for 10 h at temperature of 1900°C (*2*); load 2.5 MPa.

Fig. 6. General view of ceramic microstructure at far stages of creep. Layers: A) compressed, B) neutral, C) stretched; *a*) fracture zone, *b*) zone of porosity occurrence and crack propagation.

effect of pores and other phases (especially the vitreous phase), variations in raw materials, technology, etc.

Thus, in usual relatively short-term creep tests, only a slight modification of material structure takes place (in particular, size of crystals), i.e., structure elements existing before testing acts as dissipative elements. However long-term exposure at high temperatures perceptibly change the structure of materials, which influences creep. The migrating boundary during the growth of crystals purifies their local volumes via which is passes from the majority of impurities and pores (the same was observed in metals). As a consequence, the concentration of vacancies decreases and the creep velocity drops. Energy dissipation in recrystallization occurs through deformation due to migration of vacancies and crystal boundaries and also due to a decreasing total surface area of inner cavities (pores, microcracks), when their sizes increase. Furthermore, in the presence of large crystals, the role of boundary diffusion decreases, consequently, activation energy grows. At the same time, impurities impeding the growth of crystals can control creep in materials for a long time.

Creep in complex ceramic structures depends on its weak spot: the presence of pores and low-melting phases [17]. Pores in general can be regarded as a second (hollow) phase with zero strength. Mechanical properties depend on the size, shape, and volume content of pores (porosity). The physical
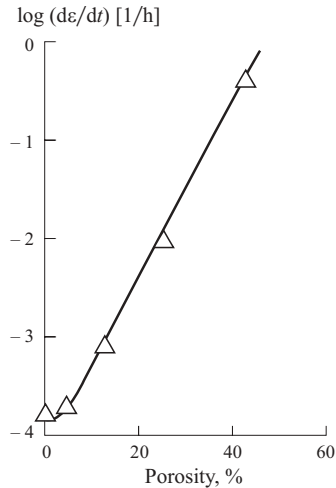
Fig. 7. Dependence of creep velocity in corundum ceramics on porosity (temperature 1500°C, load 1.3 MPa).
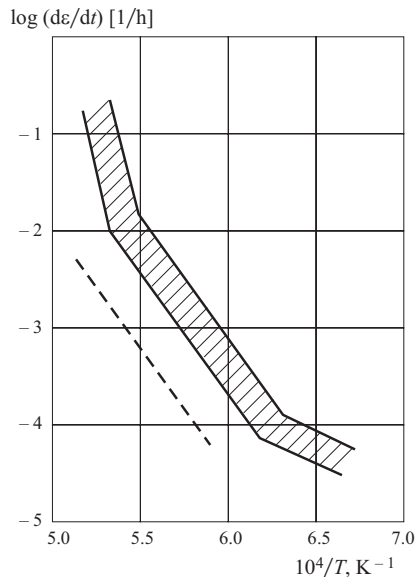

Fig. 8. Variation range of creep velocity in corundum porous (32%) ceramics depending on temperature with the mean pore size varying from 75 to 750 μm (load 1.3 MPa).

effect of pores is felt in several aspects. They decrease the effective cross-section, i.e., the surface area limited by the outer perimeter of the sample. Next, it was demonstrated [18] that destruction takes place along a complex surface passing through pores and contact sites; the contact section is significantly smaller than the effective section. Furthermore, the strength of contact is lower than that in compact material, due to an elevated content of defects in bridges between the pores compared to the grain volume. This decrease is ambiguous and related to both to physical (concave surface) and technological factors.

The effect of porosity on creep in corundum ceramics is shown in Fig. 7. It can be seen that the deformation rate

within a narrow interval (up to 5 – 7%) varies insignificantly and then grows according to the exponent. Most likely with high porosity, the state of contact between grains has a great effect and determines creep in the matrix.

The stress concentration in pores related to their shape and size does not have an effect on creep. Figure 8 shows the results of testing corundum ceramics with different pore sizes (from 50 – 100 to 500 – 1000 μm) with total porosity around 32% and approximately equal crystal sizes: 5 – 10 μm. It can be seen that their creep velocity lies in a narrow interval, although the pore size varied 10 times. Similar results were obtained on porous materials both with a granular structure and with burning-out additives, i.e., regardless of the pore shape, whether spherical or slot-shaped.

The behavior of the pore-free skeleton depends on the content of impurities determining the quantity and viscosity of the low-melting or vitreous phase. With a high content and continuous distribution of this phase, its behavior determines the creep in ceramics: the high-melting phase in this case only slightly increases the apparent viscosity of material [19]. If the low-melting phase is present in the form of inclusions, its role can be interpreted in the same way as in the case of pores. It should be taken into account that this phase has non-zero strength.

Manufacturing technology has a little effect on the behavior of articles, so far as it ensures cementing filler grains by the binding component [20]. The creep is determined by the state of the structure attained as a consequence of high-temperature treatment of the intermediate article, regardless of the ways of reaching this state. If physico-chemical processes are completed in firing (leveling of component concentrations, decreasing excessive energy or pores and crystals, etc.), it is difficult to distinguish a filler grain from the binder in a structure [21]. At the same time, industrial refractories, even those made according to the same standard, have a great spread in their creep velocities, due to variations in initial materials and techniques at various factories [22]. Deformation processes in such materials are hard to analyze and its is virtually impossible to write such test results in an analytical form having a physical meaning. The data obtained show that creep mainly depends on porosity, phase composition, and the extent and perfection of the contact between the grains. Of the phases present in refractories, the vitreous phase is the most significant for creep and the deformation velocity. In a general case, it is more convenient to search empirically for an answer regarding the behavior of a particular refractory, although results on creep presented here can be used as model results for preliminary estimates.

In complex materials, the prevailing dissipation mechanism is migration, as a rule, of rather large portions of material, which determine its deformation: these sites are dissipative elements of the structure. The empirically found series of sensitivity of ceramics and refractories to structure defects in creep can be represented as follows: macropores; low-melting phase inclusions, especially vitreous phase;

micropores; crystal boundaries, especially passing through micropores, block boundaries, dislocations, vacancies. The sequence in this series is determined by the intensity of diffusion mass transfer, i.e., a concentration of vacancies near the structural elements (defects) listed above. If the diffusion mass transfer is insufficient to compensate for emerging stresses, continuity disturbances (pores, cracks) are formed.

REFERENCES

1. V. S. Bakunov, "Specifics of high-temperature creep in ceramics," *Ogneup. Tekh. Keram.*, No. 12, 2 – 6 (1997).
2. V. S. Bakunov and A. V. Belyakov, The problem of analysis of ceramic structure," *Neorg. Mater.*, **32**(2), 243 – 248 (1995).
3. D. N. Poluboyarinov and V. S. Bakunov, "A study of creep in ceramics based on pure aluminum and magnesium oxides," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **1**(3), 373 – 379 (1965).
4. V. S. Bakunov, "High-temperature creep of refractory ceramics," *Ogneupory*, No. 6, 2 – 8, No. 7, 12 – 17, No. 8, 5 – 12, No. 9, 2 – 8, No. 10, 2 – 6, and No. 11, 2 – 8 (1994).
5. V. S. Bakunov, E. A. Voshchakin, K. I. Ryabtsev, et al., "A plant for studying thermomechanical properties of refractory materials in four-point bending," *Ogneupory*, No. 2, 39 – 43 (1975).
6. V. N. Chebotin, *Physics of Solids* [in Russian], Khimiya, Moscow (1982).
7. V. S. Ivanova, A. S. Balankin, I. Zh. Bunin, et al., *Synergism and Fractals in Material Science* [in Russian], Nauka, Moscow (1994).
8. I. Prigogine and D. Kondepudi, *Contemporary Thermodynamics. From Thermal Engines to Dissipative Structures* [Russian translation], Mir, Moscow (2002).
9. D. Dorn and D. Mote, "Physical principles of creep," in: *New Materials and Methods for Studying Metals and Alloys* [Russian translation], Metallurgiya, Moscow (1966), pp. 248 – 328.
10. V. M. Gulaev, V. S. Bakunov, D. N. Poluboyarinov, et al., "A method for identifying areas of existence of different physical mechanisms of creep in ceramic materials," *TOKhT*, **7**(5), 804 (1973).
11. D. N. Poluboyarinov, V. M. Gulaev, V. S. Bakunov, et al., "Areas of effect of various creep mechanisms in corundum ceramics," *Dokl. Akad. Nauk SSSR*, **205**(3), 653 – 655 (1979).
12. Ya. E. Geguzin, *Physics of Sintering* [in Russian], Nauka, Moscow (1967).
13. E. B. Krol' and D. N. Poluboyarinov, "Sintering and properties of mullite ceramics," in: *Publ. of NIIstroikeramika Institute, Issue 24* [in Russian], Moscow (1964), pp. 133 – 137.
14. V. S. Bakunov and A. V. Belyakov, "The effect of point defects on creep in ceramics," *Ogneup. Tekh. Keram.*, No. 5, 11 – 20 (1999).
15. V. S. Bakunov and A. V. Belyakov, "The role of crystal boundaries in diffusion creep of oxide ceramics," *Steklo Keram.*, No. 12, 14 – 18 (2001).
16. E. P. Sysoev, E. S. Lukin, and D. N. Poluboyarinov, "Creep and long-time strength of aluminum oxide ceramics," *Ogneupory*, No. 12, 34 – 37 (1976).
17. V. S. Bakunov and A. V. Belyakov, "Creep and structure of ceramics," *Neorg. Mater.*, **36**(12), 1532 – 1536 (2000).
18. M. Yu. Bal'shin, "Contact section of molded powder articles and sintered bodies and significance of their mechanical properties with respect to the contact section," *Poroshk. Metall.*, No. 4, 29 – 33 (1963).
19. I. I. Vishnevskii, E. I. Aksel'rod, and N. D. Tal'yanskaya, "High-temperature plastic deformation of amorphous-crystalline structures," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **11**(11), 2037 – 2041 (1975).
20. L. V. Sokolova, V. S. Bakunov, D. N. Poluboyarinov, and R. M. Zaionts, "Thermomechanical characteristics of aluminosilicate materials depending on their composition and structure," *Steklo Keram.*, No. 4, 22 – 23 (1976).
21. L. V. Sokolova, R. M. Zaionts, V. S. Bakunov, and D. N. Poluboyarinov, "Creep in mullite ceramics depending on its composition and structure," *Steklo Keram.*, No. 4, 22 – 23 (1976).
22. V. S. Bakunov and A. V. Belyakov, "The role of structural characteristics in high-temperature creep in ceramics," *Ogneup. Tekh. Keram.*, No. 10, 17 – 24 (2000).